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Doped Carbon Nanotubes for Hydrogen Storage

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Abstract

The ultimate goals of this research are to develop and demonstrate a low-cost hydrogen storage material that has a hydrogen capacity greater than 5.5 wt%, is stable with hydrogen cycling, and possesses favorable thermodynamic and kinetic characteristics suitable for transportation and portable devises applications. The approach to achieve these goals is to combine different solid-state hydrogen storage technologies and produce a superior hydrogen storage system. Carbon nanotube technology represents a new direction for solid hydrogen storage especially if these materials can be altered to store large amounts of hydrogen at room temperature. Modification of carbon nanotubes systems is expected to enhance and tune the hydrogen storage capabilities of the nanotubes. Carbon nanotubes were produced using different methods. Purification and high yield were achieved. Samples have been doped and spectroscopic characterization was conducted. Introducing transition metals and hydrogen bonding clusters inside these tubes can facilitate the uptake and release of hydrogen by and from the carbon nanotubes, at practical temperatures and pressures. These impeded clusters should be capable of bonding large amounts of hydrogen with favorable thermodynamics and enhanced kinetics while the transition metals catalyze the hydrogen to react with the clusters/nanotubes system.

Introduction

A major difficulty of utilizing hydrogen as fuel or energy carrier has been the absence of a practical means for hydrogen storage. Developing a high-density hydrogen storage system, above 5 weight percent, that can release hydrogen at a temperature lower than 100°C, has been the focus and the goal of researchers for years. Current approaches of hydrogen storage are compressed gas, liquid, or in the form of solid hydrogen. A solid hydrogen storage system is reliable, simple to engineer, and tremendously safer. Examples of solid hydrogen storage are metal hydrides, carbon (nanotubes, Fullerenes and activated carbon) or glass microspheres. In 1991, Sumio Iijima produced nanotubes by vaporizing carbon graphite, using an electric arc under an inert atmosphere [1]. The discovery has generated much interest and created extensive research activity into the properties and application of the nanometer-scale cylindrical carbon tubes. At first, the nanotubes were multi-layered, made up of 2 to 50 concentric cylindrical shells with outer diameters of few tens of nanometers and lengths on the order of few μm. Further research activities led by two independent efforts resulted in the development of single wall carbon nanotubes (SWNT) in macroscopic quantities. [2, 3]. It has been reported that large-diameter single wall nanotubes can be an ideal media for hydrogen storage because of their high gravimetric energy density [4]. Several research institutes and companies in the U.S. and elsewhere are exploring the use of carbon nanotubes for hydrogen storage. Single wall nanotubes technology represents a new direction for solid hydrogen storage especially if these materials can store larger amounts of hydrogen at room temperature than does graphite alone. Our objective has been to utilize the physisorption effect and generate a chemisorption effect by introducing transition metals and hydrogen bonding clusters inside the tubes. Controlling the type and size of the clusters is expected to allow us to tune the material for hydrogen sorption at desired temperatures and pressures.

Results and Discussion

It has been argued that contamination during sample preparation or during experimental measurements can produce unreliable results [5]. Precautions were taken to avoid errors or misleading data that can lead to incorrect conclusion regarding the hydrogen uptake and release by and from the carbon nanotubes. The sample preparation system, the thermodynamic characterization system, and the hydrogen uptake and release quantification system were all confined in an argon gas atmosphere glovebox connected to sensors and computer interface for control and data monitoring. Hence, the nanotubes samples can be purified, degassed, opened and doped under inert atmosphere. The samples can be then hydrided/dehydrided using a thermogravimetric analyzer (TGA) and the heat of reaction can be measured using a scanning calorimeter (DSC) without the risk of exposing the samples to contamination. SWNT samples provided by Dr. Ching-Hwa at UCLA were prepared by carbon evaporation in the presence of metal catalysts [6,7]. Samples were purifeid and characterized by SEM. Several purification schemes were applied to remove impurities from SWNT. For example, SWNT samples were exposed to oxidative environment. Samples were washed out in acid to remove metal particles. See Fig 1a., 1b.

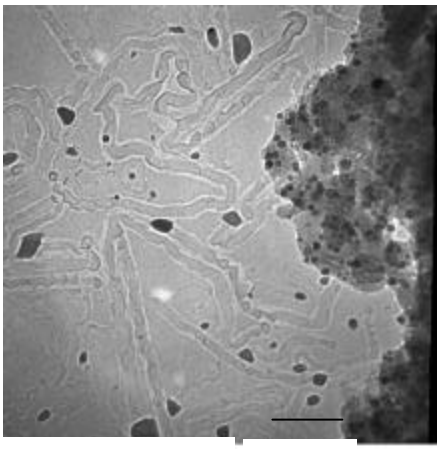

Fig 1.a SWNT sample as received

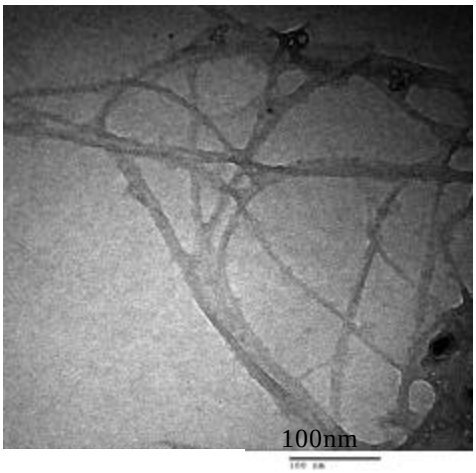

Fig1.b SWNT sample after purification

In collaboration with Dr. Apparao M. Rao at Clemson University (SC), other samples were prepared using CVD methods. The metal particle and nanotubes were created in a uniform configuration that can be controlled. These types of samples can be prepared in large quantities. See Fig. 2.

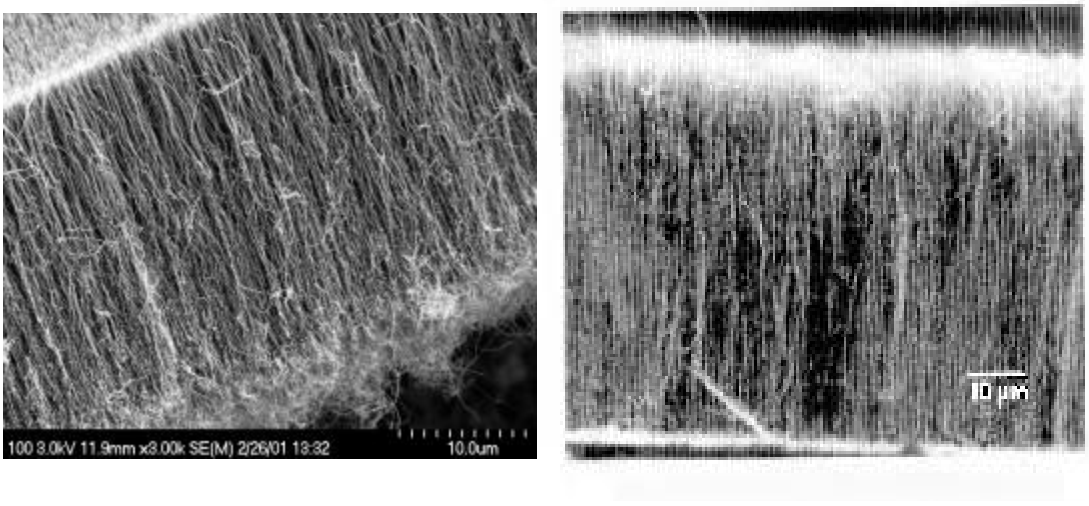

Fig. 2 Samples prepared by CVD methods showing the metal particles at the top of the nanotubes

The samples were characterized using (TEM) microscopy to determine the size of the tubes and the impeded metal particles. See Fig. 3 [8].

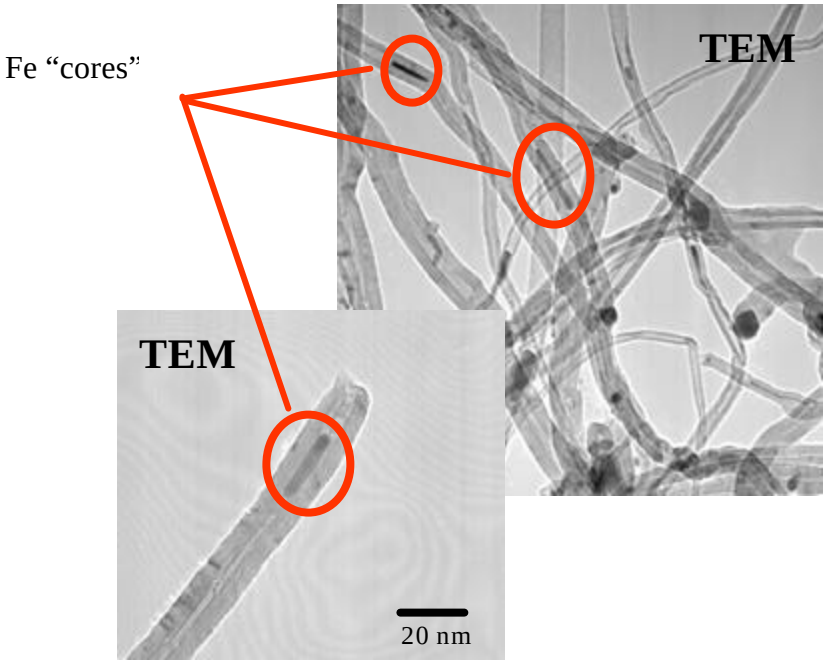

Fig. 3 TEM Images of Nanotubes grown from ferrocene saturated xylene-ferrocene mixtures [8]

Conclusions

Our immediate plan was to establish a state of the art capability for synthesizing, modifying and doping carbon nanotubes for hydrogen storage as well as to establish reliable means for characterizing these materials. The characterization effort involved material characterization using spectroscopic measurements (SEM, TEM, and EDS). Hydrogen sorption characterization systems (e.g. TGA, TVA, and DSC) were enclosed in an inert atmosphere to avoid the possibility of contamination. Our objective was aimed at producing large quantities of pure carbon nanotubes that represent a practical sample of material. We felt that large quantities of consistent structures, that can be modified as needed, were required to avoid discrepancy in the data. Consequently, through different means of synthesis, high purity samples were obtained. The samples were doped with metals as planned.

Future Work

In order to determine the hydrogen sorption performance of these carbon nanotubes preliminary Thermal Desorption Spectrum (TPD) measurements will be performed on samples, using thermovolumetric and thermogravimetric systems. The rate of hydriding and dehydriding will be obtained at fixed temperatures and pressures. The stability of the doped SWNT with cycling will be determined. The thermodynamic characteristics of samples will be obtained. The type and size of nanotubes and clusters that result in a reversible high hydrogen capacity will be

identified. The effect of contaminants on the performance of hydrogen uptake and release and the capacity of hydrogen will be investigated

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